

**ATTACHMENT 1****PATENT ABSTRACTS OF JAPAN**

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SAITO SOKI**(54) FRESHNESS RETAINING AGENT****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To obtain a freshness retaining agent capable of preventing the discoloration of a raw vegetable and suppressing the propagation of microorganisms sticking to the vegetable and suitable for preserving the cut vegetable, etc., by including hinokitiol, chitosan and ethanol.

**SOLUTION:** This freshness retaining agent contains hinokitiol in an amount of preferably 5.0-20 wt.% (based on ethanol), chitosan in an amount of preferably 0.005-10 wt.% (based on the ethanol) and the ethanol. Vegetables are preferably brought into contact with an aqueous solution prepared by diluting the freshness retaining agent to 0.1-10 wt.% to carry out the sterilizing treatment of the vegetables or preferably brought into contact with an aqueous solution containing chlorine dioxide and then coated with the freshness retaining agent to conduct the sterilization treatment of the vegetables. Naturally occurring hinokitiol, an alkali metal salt of hinokitiol, an iron complex, etc., of the hinokitiol are preferably used as the hinokitiol.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the freshner used in order to make the freshness of greenstuff hold, and its usage.

[0002]

[Description of the Prior Art] In recent years, in eating habits, the needs for the convenience of the ease of treating in the ease of asking are increasing with diversification of a life style. This is being able to say also about greenstuff and the inclination to ask for processed vegetables, such as cut vegetables already processed to some extent at the time of purchase, for simple nature, rationality, and economical efficiency from viewpoints, such as processing of the preservation after purchase, the complicatedness of cooking, and the waste after cooking, is becoming strong. However, compared with the fresh vegetables into which it is not processed at all since the physiological change accompanying cutting of vegetables in greenstuff, such as cut vegetables, is sharp, decomposition tends to advance [ a freshness fall ] early.

[0003] This problem is coped with, transformation of vegetables and deterioration are avoided from the former, it considers as the method of carrying out freshness maintenance of the various methods for holding freshness, for example, greenstuff, and the fruits, and there is the method of processing with germicides, such as the method of using an ethylene adsorbent, the method of using the packing material which made the antimicrobial agent contain, and a sodium hypochlorite, etc.

[0004] It generates by vegetable aging process and ethylene is carrying out the operation which brings forward the advance to the aging to garden stuff, it is the matter soon led to \*\*\*\*\*, and there are what carries out an adsorption treatment with porosity objects, such as activated carbon, and a thing to depend on the method of decomposing with a catalyst in an ethylene remover.

[0005] However, since an ethylene adsorbent aims at removal of ethylene, an antibacterial effect over the various germs adhering to vegetables cannot be desired. It is necessary to discard an ethylene adsorbent after use, and it has the fault which causes the increase in industrial waste. Moreover, since an ethylene adsorbent demonstrates an effect by using together with plastic film, it must process these as waste after use. Moreover, there are some which noble metals, such as palladium, contain in the catalyst for ethylene decomposition, and we are anxious about the problem which cost not only increases at the time of manufacture, but carries out soil pollution at the time of waste treatment arising.

[0006] As other methods of holding the freshness of vegetables, the technology of pressing down propagation of the various germs on the front face of a vegetable is indicated by packing vegetables by the packing material which made the safe antimicrobial agent contain. For example, although the method using the thing which made wrapping, such as a resin film, contain the cyclodextrin clathrate compound containing hinokitiols is indicated by JP,61-108359,A, since the effect of the freshness maintenance by the method of starting will be restricted to a contact portion with a packing material, in the case of cut vegetables, there is almost no effect in \*\*\*\* prevention of a cutting plane.

[0007] As other main methods of holding vegetable freshness, the method of processing with chlorine-

based germicides, such as a sodium hypochlorite, can be mentioned. However, when this germicide is used, the process for fully washing the germicide adhering to vegetables is required. Thus, although the various germs which adhered to vegetables immediately after carrying out sterilization processing are decreasing remarkably, it is deficient in the effect which prevents propagation of various germs during subsequent preservation, i.e., an antibacterial effect. That is, although bacteria decrease in number at once, since the germicide adhering to vegetables fails to be poured, it breeds after that. Or the floating various germs adhere to a vegetable front face, and breed.

[0008]

[Problem(s) to be Solved by the Invention] It aims at holding freshness by this invention's relating to the freshner suitable for the use to fresh vegetables, especially the cut vegetables, preventing discoloration of fresh vegetables, and preventing the propagation of a microorganism adhering to vegetables.

[0009]

[Means for Solving the Problem] By processing fresh vegetables in the solution which consists of chitosan, a hinokitiol, and ethanol, this invention is characterized by preventing discoloration of fresh vegetables and preventing decomposition, and has a remarkable effect to the cut fresh vegetables. Although especially the greenstuff set as the object of this invention is not restricted, these cut vegetables, such as the lettuce with which the injury by the passage of time poses a quality maintenance top problem early, a cabbage, parsley, Chinese cabbage, a spinach, and Japanese honewort, are mentioned. Since the cellular structure is destroyed by shredding, a microorganism tends to breed and, especially as for cut vegetables, the fall of freshness advances quickly by contamination accompanying it.

[0010] The freshner in which the freshner which added the organic acid to hinokitiol content alcohol, and adjusted pH to it contained at least one sort chosen as JP,2-222645,A from ethanol, a sorbitol, glycerols, and the organic acid becomes JP,6-125704,A from vinegar, ethyl alcohol, and chitosan, and the freshner which made the organic acid contain as a pH regulator by the case is taught to JP,2-5822,A. The freshner of JP,2-5822,A makes vinegar, ethyl alcohol, and chitosan the indispensable requirements for composition. It needed to be used, after carrying out remarkable dilution of the undiluted solution, in order pH is too low for food, and to invite the wilt of fresh vegetables to it, using these as it is and to reduce the unpleasant odor of vinegar. However, if each aforementioned component was little, since an antibacterial effect was not expectable, the effect of an antibacterial effect becoming weaker, fully decreasing the number of micro organisms immediately after processing, and suppressing propagation of a bacillus by dilution was inadequate.

[0011] As a result of inquiring wholeheartedly to the above-mentioned trouble, by processing vegetables, especially cut vegetables in the solution which consists of chitosan, a hinokitiol, and ethanol, this invention persons prevented discoloration of fresh vegetables, found out that the vegetables with which the freshness fall which reduces propagation of various germs cannot take place easily were obtained, and resulted in this invention.

[0012] As a hinokitiol used for this invention, potassium salt, the alkali-metal salt, for example, the sodium salt, of a natural hinokitiol and a hinokitiol, etc. can use the iron complex of a hinokitiol. A hinokitiol component is little, and since it has antibacterial, it is an effective component for preventing that various germs breed to vegetables and holding freshness. The freshner of this invention can be made to be able to contain chitosan as an indispensable component, and can be made to demonstrate the effect of the above-mentioned hinokitiol component effectively over a long period of time. Since there is antimicrobial activity in chitosan and antimicrobial activity is demonstrated over a long period of time, a fresh object can be protected from decomposition. Moreover, since chitosan has the operation which forms a coat, when the coat of the chitosan containing the above-mentioned hinokitiol coats the cutting plane of vegetables, proliferation of the various germs which prevent the oxidization with the air under preservation or browning by the enzyme, and cause rotten can be pressed down, and freshness maintenance can be carried out over a long period of time.

[0013] Since it is refractory, each hinokitiol is used for water in the solution containing ethanol like JP,2-5822,A, dissolving. Although antibacterial is high even when a hinokitiol is little, since it is easy to

volatilize, it is difficult to maintain antibacterial over a long period of time. Moreover, since the ethanol which is a solvent also has high volatility, although the number of micro organisms decreases immediately after processing, a bacillus tends to breed after that. Therefore, the amount used needed to be made [ many ]. Then, when chitosan was used for fresh vegetables as a component of indispensable composition, the durability of not only the antibacterial effect under preservation but the browning prevention effect is improvable by leaps and bounds. In this invention, the durability of the browning prevention effect under preservation and an antibacterial effect is improved by leaps and bounds with the combination of chitosan, a hinokitiol, and ethanol. That is, since the coat of chitosan coats fresh vegetables where a hinokitiol is subsumed, the hinokitiol component which is easy to volatilize is held and the antibacterial effect of a hinokitiol component is demonstrated over a long period of time. Although there was antibacterial [ continuous ] in chitosan, sterilizing properties were lows compared with ethanol or the hinokitiol, and when chitosan was used as a freshness maintenance component, they needed to make [ many ] the amount used. On the other hand, since chitosan subsumes a hinokitiol and it not only acts as an antibacterial component, but coats fresh vegetables with this invention, the hinokitiol component which is easy to volatilize is held stably, and an antibacterial effect and the browning prevention effect can be demonstrated over a long period of time by use of a little hinokitiol and little chitosan. Moreover, since little use of the thing water-soluble as chitosan to be used is only carried out, when dissolving a lot of chitosan, it does not require using organic acids, such as required vinegar, (in JP,6-125704,A, although vinegar is made into the requirements for indispensable composition, this is a shell which chitosan tends to dissolve in organic-acid solution).

[0014]

[Embodiments of the Invention] In order to carry out this invention, a hinokitiol and chitosan are first dissolved in the alcoholic tablet containing ethanol. To the ethanol contained in the alcoholic tablet used as a solvent, the hinokitiol at this time and the concentration of chitosan prepare the undiluted solution of a freshner so that it may become 5.0 - 20 % of the weight, and 0.005 - 10% of the weight. As an organic solvent for dissolving a hinokitiol and chitosan, although ethanol is desirable, since it is directly used for food, the alcohol for a brewing which makes ethanol the principal component is desirable. Moreover, it not only has a function as a solvent, but since ethanol has the sterilization effect, it uses it as a constituent of the freshner in this invention.

[0015] By contacting what diluted the prepared undiluted solution of a freshner with the solution of water and others as it was on vegetables or a fruits front face, the freshner of this invention can prevent change of a color tone, and can demonstrate the freshness maintenance effect. When diluting and using the undiluted solution of a freshner for solution, it is desirable to prepare and use a content so that the concentration of a hinokitiol, chitosan, and ethanol may not be less than  $5.0 \times 10^{-3}$  % of the weight,  $5.0 \times 10^{-6}$  % of the weight, and 0.1 % of the weight to the solution at the time of use, respectively. The freshner of this invention is because the freshness maintenance effect cannot fully demonstrate when the content of these components is less than the aforementioned range, although a hinokitiol, chitosan, and ethanol are made into an indispensable constituent.

[0016] The freshness maintenance method of \*\*\*\*\* permeates the solution which diluted the above-mentioned freshner for about 1 - 10 minutes after washing vegetables using the freshner of this invention. Or spray processing of what diluted the undiluted solution of the above-mentioned freshner with the solution of remaining as it is, or water and others is carried out on the surface of vegetables. Or the freshner of this invention can also be used as mentioned above besides using it for food independently, using it together with the conventional sterilization method. For example, as the method of sterilization processings, such as cut vegetables, although use of the above-mentioned chlorine-based germicide is common practice, after performing sterilization processing by these chlorine-based germicides, propagation of the viable cell after sterilization can be suppressed very effectively by carrying out after treatment, such as an application or being immersed, for the freshner of this invention further.

[0017] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. In addition, in each example, % should be displayed in weight %.



[0018]

[Example] The alcohol for a brewing of the manufacture natural hinokitiol of a [example 1] (1) freshner, chitosan, and 75% of ethanol concentration was used, and the undiluted solution of the freshner of the freshner of this invention and its example of comparison, and the example of contrast was prepared. The composition is shown in Table 1.

[0019]

[Table 1]

	ヒノキチオール (%)	キトサン (%)	醸造用アルコール (エタノール濃度 75%)	水道水 (%)	食酢 (酸度10%)
本発明溶液1	1.0	0.0005	10.0%	残部	0
本発明溶液2	0.5	0.1	1.0%	残部	0
比較例1	2.0	0	10.0%	残部	0
比較例2	0	2.0	10.0%	残部	0
比較例6	0	2.0	5.0	残部	5.0
比較例7	0	2.0	0	残部	5.0
比較例8	0	2.0	5.0	残部	5.0
対照例	0	0	0%	100	0

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[0020] (2) The example 5 (freshness maintenance film) of comparison

For comparison with the freshner of this invention, the freshness maintenance film was manufactured as follows and it considered as the example 5 of comparison. Cyclodextrin 1.5g was dissolved in 100ml of water, and hinokitiol 0.2g was added, it stirred at about 60 degrees C, and the precipitate of an inclusion object was obtained. Subsequently, this precipitate was extracted, it freeze-dried and the cyclodextrin inclusion compound of a hinokitiol was obtained. 50g of 1.0% concentration suspension solution of this inclusion compound was uniformly applied to polyethylene film 1m<sup>2</sup>, it was air-dry at about 40 degrees C, and the freshness maintenance film (example 5 of comparison) was obtained.

[0021] [Example 2] (aging examination)

(1) About the freshner of this invention tablets 1 and 2 of the processing table 1 by the freshner of Table 1, the examples 1 and 2 of comparison, and the example of contrast, 1l. of ion exchange water was added to 10ml, respectively, and the processing agent of dilution was made 100 times. Hereafter, an example 1 and an example 2 are made into Example 1 and Example 2, respectively, and let the processing agents which diluted the aforementioned examples 1 and 2 be Example 3 and Example 4, respectively. Moreover, the processing agent which diluted the aforementioned examples 1 and 2 of comparison is explained below as the example 3 of comparison, and an example 4 of comparison, respectively. It was immersed for about 10 minutes into each processing agent 2l., and sterilization processing of about 160g cut lettuce cut and washed was carried out. Cut lettuce [ finishing / this sterilization processing ] was cut underwater and packed, subsequently it saved at 10 degrees C, and aging of the color of cut lettuce was observed. In addition, the criteria of evaluation of aging are carried out as follows.

- : -- discoloration -- there is nothing -- normal \*\*: -- a little -- discoloration +: brown -- discoloration ++: about 160g lettuce which it discolored brown, and the use cut of the freshness maintenance film of the example 3 of (2) comparison which senses a nasty smell was carried out, and was washed -- the freshness maintenance film of the example 3 of comparison -- using it. It packed, and, subsequently saved at 10 degrees C, aging of the color of cut lettuce was observed, and aging was evaluated like the case of processing by the above-mentioned freshner.

(3) The result of the result table 2 of the freshness maintenance effect shows that what was processed in this invention tablet or the examples 1 and 2 of comparison has good keeping of freshness since there is all little aging as compared with the example of contrast. Since the freshness maintenance effect will be limited only to a contact portion with a film in the case of the example 3 of comparison which used the freshness maintenance film, the freshness maintenance effect did not show up into the portion which did not contact a film, but the freshness maintenance effect became of the same grade as the example of contrast as a whole. On the other hand, although the freshner of this invention was used, a result understands a bird clapper still better as compared with the freshner of ethanol, hinokitiol combination, or ethyl alcohol and chitosan combination. Thus, it turns out that the freshness maintenance effect of the freshner of this invention improves further according to the synergistic effect of a hinokitiol and chitosan.

[0022]

[Table 2]

	スタート	1日後	2日後	3日後
例1	—	—	—	±
例2	—	—	—	±
例3	—	—	—	±
例4	—	—	—	±
比較例1	—	±	+	++
比較例2	—	±	+	++
比較例3	—	±	+	++
比較例4	—	±	+	++
比較例5	—	+	++	++
比較例6	—	±	+	++
比較例7	—	±	+	++
比較例8	—	±	++	++
対照例	—	+	++	++

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[0023] [Example 3] (the browning prevention effect examination)

As mentioned above, compared with the case where it processes in the example of contrast, the preservative of this invention has the high effect of preventing discoloration of vegetables. then, about the effect over the cut end of vegetables with the most intense freshness degradation, above-mentioned Example 3 and the above-mentioned example of contrast were used and the browning prevention effect was checked as follows to confirm this effect further First, above-mentioned Example 3 and the above-mentioned example of contrast were used, and the stalk cutting plane of lettuce was processed, respectively. Subsequently, while taking a photograph of the lettuce stalk cutting plane on the 3rd after processing and measuring lightness, comparison of the browning degree by visual observation was also performed. In order to measure lightness, photography took a photograph of the stalk cutting plane of lettuce, and a standard color color tone board together. Incorporation was performed for this photograph to the computer using picture incorporation scanner equipment (product made from EPSON), with image-analysis software (Image-Pro Plus), the color was amended from the standard color color tone, and RGB analysis was performed about the stalk cutting plane of lettuce after that. Thus, the browning degree of the freshner of this invention and the example of contrast was compared like the above by measuring the lightness of the stalk cutting plane of lettuce using a photograph, and measuring lightness. Lightness measurement was divided into three colors of the red who is the three primary colors of light,